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THE ISOLATION OF SOME OF THE CHEMICAL CONSTITUENTS OF PETROLEUM

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

JOHANNES H. BRUUN

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THE ISOLATION OF SOME OF THE CHEMICAL CONSTITUENTS OF PETROLEUM

INTRODUCTION

DURING the past sixty or seventy years much work has been done on the composition of petroleum obtained from various parts of the world, and many investigators, notably Pelouze, Cahours, Schorlemmer, Markownikow, and Mabery, have attempted to isolate the chemical constituents in different petroleum fractions. However, a search through the literature shows that our knowledge of this subject at present is extremely meager. The reason for this is well explained by Professor Gurwitsch[1] in the introduction to his last book, as follows:

"The great variety and the unusually complex chemical composition of petroleum oils cause the detailed investigation of their constituents to be one of the most difficult problems of chemistry. The separation and isolation in a chemically pure state of these substances is most difficult, and in many cases has, up to the present, been found impossible not only because the most varied chemical groups such as hydrocarbons, acids, phenols, bases, sulphur compounds, etc., are present but also because so many isomeric and homologous compounds present themselves in each group."

In previous work a number of different methods of attacking the problem have been used. Pelouze and Cahours[2] used fractional distillation and chemical treatment with fuming sulphuric acid and sodium hydroxide.

In place of sulphuric acid Schorlemmer[3] used concentrated nitric acid while Lemoine[4] used bromine for the separation of unsaturated compounds.

[1] "Wissenschaftliche Grundlagen der Erdölverarbeitung," L. Gurwitsch, p. 1, Julius Springer, Berlin, 1924.

[2] Compt. rend., **56**, 505 (1863); **57**, 62 (1863).

[3] Lieb. Ann. d. Chem., **161**, 263 (1871).

[4] Bull. de la Soc. de chim., Paris, **61**, 161 (1884).

Markownikow[5] and his assistants in their extensive work on Caucasian petroleum used the following treatments in succession:

(1) Fractional distillation.
(2) Refining with fuming sulphuric acid by which the unsaturated hydrocarbons and asphaltic substances were mainly eliminated.
(3) Treatment with a mixture of sulphuric acid and fuming nitric acid in order to convert the aromatic hydrocarbons into the difficulty soluble dinitro compounds. In many cases in which this treatment is insufficient, Markownikow recommends oxidation of the distillate with very strong nitric acid at 0°C. by which, however, the naphthenes are attacked.
(4) Washing the fractions with sodium hydroxide solution after nitration, and distilling off from the nitro compounds.
(5) 20 to 30 fractional distillations.

Engler[6] and his co-workers used a concentrated aqueous solution of mercury acetate for removing unsaturated hydrocarbons with which the acetate forms double compounds. By means of formaldehyde and sulphuric acid the aromatic hydrocarbons were then converted into the so called formolites, thus leaving a mixture of pentamethylenes, naphthenes and paraffin hydrocarbons. By conducting these vapors over nickel at 300° or palladium black at 200°C. the naphthenes (hexamethylene compounds) are converted into aromatic hydrocarbons which may be separated in the form of formolites. The remaining pentamethylenes and paraffin hydrocarbons are then separated by repeated fractional distillation.

The process of Edeleau depends upon differences in the solubilities of aromatic, unsaturated and paraffin hydrocarbons in liquid sulphur dioxide.

A general objection to all of the methods for determining the composition of petroleum (with the possible exception of Edeleanu's process) is the destructive influence of the chemical reagents upon some of the constituents. Although pure paraffin and naphthene hydrocarbons are usually neither attacked nor dissolved by concentrated sulphuric acid, the case is different when substances are present that are attacked or dissolved by this acid. Even normal hexane, heptane, and octane may be partly sulphonated by fuming sulphuric acid,[7] and with naphthenes simultaneous oxidation and sulphonation may take place.[8] A

[5] Zuzammenfassende Veröff J. Russ. Phys.-Chem. Soc. Chem. Pt., 1883 and Lieb. Ann., 301, 157 (1898).

[6] See p. 4 of reference 1.

[7] Worstall, Am. Jour. Chem., **23**, 654 (1898).

[8] Markownikow, J. Russ. Phys.-Chem. Soc., 141 (1892).

strong objection may also be made against using nitric acid treatment for the separation of aromatic from aliphatic hydrocarbons. Although the normal and quaternary hydrocarbons are very resistant to this acid, the secondary and tertiary hydrocarbons react easily with evolution of heat and the formation of carbonic acid, lower acids, and tertiary nitro-derivatives.[9]

The formolite reaction as used by Engler seems to be efficient for the removal of the aromatic hydrocarbons, but has the objection that these hydrocarbons will be lost for further investigation, as they can not be recovered from the formolite compounds.

Concerning actual results obtained by previous investigators, E. W. Washburn[10] has summarized this briefly in stating:

"An examination of the literature on the composition of petroleum discloses the reported existence of a large number of different hydrocarbons to which formulas and values of physical properties have been assigned. A study of the evidence presented in identification of these 'compounds,' however, impresses one chiefly because of its inadequacy. In fact, with the exception of some of the lower boiling constituents, most of the compounds whose existence has been reported must be classed as purely fictitious in the light of the evidence at present available."

As mentioned above, the destructive influence of the chemical reagents used by previous investigators makes it impossible to include all classes of hydrocarbons in one analysis. It is therefore desirable to omit any chemical treatment which would destroy certain groups of hydrocarbons or only convert them into new compounds from which the hydrocarbons could not be recovered in their original form. For this reason it has been found advisable to make use only of such methods as the following:

(1) Distillation at atmospheric pressure (for compounds with low boiling points only).
(2) Distillation by means of inert gas or steam.
(3) Distillation in vacuo.
(4) Distillation in molecular stills.[11]
(5) Distillation after the addition of a component which forms constant-boiling mixtures with some of the hydrocarbons and which afterwards can be separated easily from the hydrocarbons by, for instance, extracting with water.
(6) Fractional crystallization or equilibrium melting.

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[9] Markownikow, Ber., 1445 (1899).
[10] Bur. of Stds. J. of Research, **2**, 468 (1929).
[11] Washburn, Bur. of Stds. J. of Research, **2**, 476 (1929).

(7) Practical application of the partition law by extraction with a solvent which afterwards can be separated from the petroleum fraction either by distilling or by washing with water.

I. THE EFFECT OF HIGH TEMPERATURES UPON PETROLEUM IN THE PRESENCE OF HYDROGEN, NITROGEN, OR CARBON DIOXIDE

In order to prevent the higher boiling constituents of petroleum fractions from breaking down ("cracking") it was decided to carry out the first distillation in an atmosphere of inert gas. Preliminary experiments were made with different inert gases to determine their effect upon the

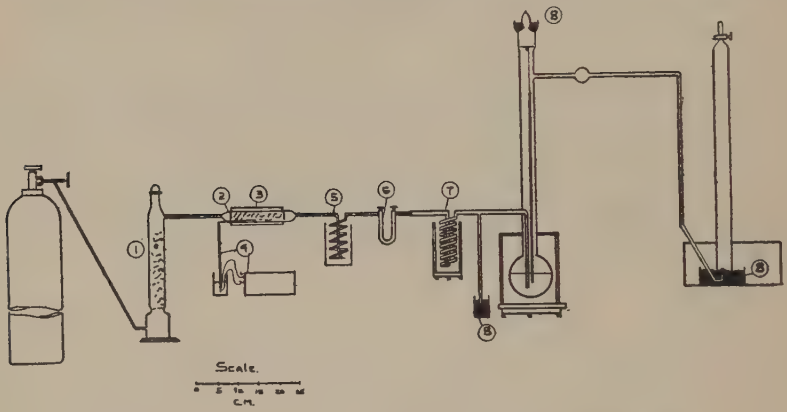

FIG. 1. APPARATUS FOR STUDYING CRACKING BEHAVIOR

tendency of the oil to crack at the temperatures employed in the distillation.

These experiments were carried out in the apparatus shown in Fig. 1. The entire assembly is made of pyrex glass. The gas is first purified, preheated, and then passed continuously into the oil, which is heated to definite temperatures during different intervals of time. The amount of cracking is estimated by comparing the iodine numbers of the oil before and after subjecting it to this treatment. The inert gas passes from its storage cylinder through a drying tower, *1*, filled with magnesium perchlorate trihydrate ($Mg(ClO_4)_2 \cdot 3H_2O$) and then into an electrically heated furnace, *2*, containing copper shavings (temperature 650°C.) for the removal of oxygen. A cooling coil, *5*, is placed next in the train, and this is followed by a second drying tube, *6*. The gas is then preheated, *7*, and bubbled into the flask containing the oil in contact with

copper and brass turnings. A mercury-seal safety valve, *8*, is placed between the heater and the flask, thus taking care of any excess pressure.

The inert gas is first allowed to bubble through the oil at room temperature for two hours in order to free it from dissolved or occluded gases or water vapor. The temperature is read from a thermometer suspended in the flask. The flask is provided with a reflux column kept at room

TABLE 2

Cracking behavior of refined wax (containing 0.09 per cent of sulphur) in the presence of CO_2 during heating for 20 hours at various temperatures*

t	Iodine number		
	Before	After	Increase
°C.			
200	11.4	11.5	0.1
250	11.4	11.4	0.0
320	11.4	11.5	0.1
360	11.4	16.7	5.3

* The raw-wax fraction contained 0.28 per cent of S. After washing with concentrated H_2SO_4 this was reduced to 0.09 per cent. At the same time the iodine number fell from 16 to 11.4.

TABLE 3

Effect of CO_2 in presence of Fe, FeO and Fe_2O_3—variation with temperature for a 20-hour heating period

t	Iodine number		
	Before	After	Increase
°C.			
310	11.0	11.0	0.0
320	11.0	11.9	0.9
330	11.0	13.7	2.7

temperature, using an air blast when necessary. A cotton-filled bulb in the gas outlet at the top of the column frees the gas from any oil spray, and the gas is then forced through a mercury seal. The hydrogen and nitrogen are allowed to escape, but the carbon dioxide is absorbed in a tower containing a strong solution of potassium hydroxide. Using a wax distillate from No. 6 well of the South Ponca Field, Kay County, Okla., the results obtained are given in Table 1.

TABLE 1

Cracking behavior of raw-wax fraction in the presence of various gases

Effect of nature of gas—three hours' heating at 370°C.

Gas	Iodine number		
	Before	After	Increase
N_2	16.0	17.5	1.5
H_2	16.0	17.4	1.4
CO_2	16.0	17.2	1.2

Effect of CO_2—variation with time of heating at 370°C.

Time	Iodine number		
	Before	After	Increase
hours			
0.5	16.0	16.4	0.4
3	16.0	17.2	1.2
20	16.5	21.5	5.0

Effect of CO_2—variation with temperature for a 20-hour heating period

t	Iodine number		
	Before	After	Increase
°C.			
100	16.5	16.6	0.1
200	16.1	16.1	0.0
250	16.7	16.8	0.1
315	16.4	16.8	0.4
350	16.7	19.4	2.7
370	16.7	21.5	5.0

Effect of boiling in contact with air for 20 hours under a return condenser

B.p.		Iodine number		
Initial	After 20 hours	Initial	After 20 hours	Increase
°C.	°C.			
370	330	16.3	59.1	42.8

The experiments shown in Table 2 were all carried out in the presence of brass and copper shavings, as the still which was used first was made of these materials. Later, it was thought preferable to build a still of steel. Also some experiments were carried out in order to investigate the catalytic influence of iron and iron oxides upon the cracking of hydrocarbons in an unrefined "raw wax" fraction from the same well.

From the results shown in Table 3 it is clear that in the presence of these inert gases little change in the iodine number occurs during pro-

TABLE 4

Chemical treatment of the raw-wax fraction from an Oklahoma crude

Chemical treatment	Per cent S	Iodine number
None	0.28	16.0
I. Shaken with		
(a) $\frac{1}{20}$ vol. H_2SO_4 100% 3 times		
(b) 1 vol. water		
(c) $\frac{1}{20}$ vol. NaOH 100 g./L.		
(d) 1 vol. water		
Dried over $CaCl_2$ and filtered	0.07	10.1
II. Shaken with		
(a) $\frac{1}{20}$ vol. H_2SO_4 100% 2 times		
(b) 1 vol. water		
(c) $\frac{1}{20}$ vol. NaOH 100 g./L. 2 times		
(d) 1 vol. water		
Dried over $CaCl_2$ and filtered	0.09	11.4
III. Refluxed with metallic Hg in CO_2 atm. 20 hrs	0.27	16.2
IV. Refluxed over metallic copper in CO_2 atm. 20 hrs	0.27	21.5
V. Refluxed over metallic copper in presence of air 20 hrs.	0.26	59.1

longed heating up to 320°C. and even at 370° the iodine number increases only one unit as a result of heating for three hours.

II. EFFECTS OF VARIOUS CHEMICAL TREATMENTS UPON THE SULPHUR CONTENT AND IODINE NUMBER OF HIGHER PETROLEUM FRACTIONS

For the purpose of investigating the possibility of removing sulphur compounds and unsaturated hydrocarbons from the oil before subjecting it to fractional distillation various chemical treatments were tried (Tables 4 and 5).

The data in Tables 4 and 5 show that of the chemicals used 100 per cent sulphuric acid seems to be the most efficient reagent for the removal of unsaturated hydrocarbons as well as sulphur compounds. However,

this acid is very objectionable to use, if a complete separation of the constituents of petroleum is desired, as large quantities (from 10 to 35

TABLE 5

Chemical treatment of the gas-oil fraction from an Oklahoma crude

Chemical treatment	Per cent S	Iodine number
None	0.11	10.9
I. Shaken with		
(a) Metallic Hg		
(b) Water		
Dried over $CaCl_2$ and filtered	0.12	10.4
II. Shaken with		
(a) ½ vol. of mercuric acetate 250 g./L.		
(b) Water		
Dried over $CaCl_2$ and filtered	0.12	10.3
III. Shaken with		
(a) ½ vol. of mercuric chloride 50 g./L.		
(b) 1 vol. water		
Dried over $CaCl_2$ and filtered	0.12	10.3
IV. Shaken with		
(a) $\frac{1}{20}$ vol. of H_2SO_4 95%		
(b) Water		
Dried over $CaCl_2$ and filtered	0.075	9.3
V. Shaken with		
(a) $\frac{1}{20}$ vol. of H_2SO_4 95%		
(b) 1 vol. water		
(c) $\frac{1}{10}$ vol. NaOH 200 g./L.		
(d) 1 vol. water		
Dried over $CaCl_2$ and filtered	0.08	9.5
VI. Shaken with		
(a) $\frac{1}{20}$ vol. H_2SO_4 95%		
(b) 1 vol. water		
(c) $\frac{1}{10}$ vol. NaOH 200 g./L. + PbO 10 g./L.		
(d) 1 vol. water		
Dried over $CaCl_2$ and filtered	0.07	9.7
VII. Shaken with		
(a) $\frac{1}{20}$ vol. of H_2SO_4 100% 4 times		
(b) 1 vol. water		
(c) $\frac{1}{10}$ vol. NaOH 200 g./L. 4 times		
(d) 1 vol. water		
Dried over $CaCl_2$ and filtered	0.025	6.8

per cent by volume) of the oil are removed and converted to a black residue. For this reason, it was decided to carry out the distillations with-

out previous refining, especially as the content of sulphur and unsaturated compounds in the petroleum fractions obtained from Oklahoma is very low (as indicated by a sulphur analysis and by a low idodine number).

III. RECTIFYING COLUMNS WITH NON-SIPHONING BUBBLING CAP PLATES

From a study of the problems of separating constituents of petroleum and of the boiling points of the hydrocarbons and their isomers, it is apparent that the separation of these compounds by fractional distillation can be accomplished only by using rectifying columns of a very high degree of efficiency. In order to obtain a separation, the distillation must be carried out at a low speed, using a large reflux ratio, and with the intermittent addition of liquid to the still pot. As the distillation, therefore, will have to be extended over a long period of time the need of a rectifying column with the following properties is apparent:

It should be possible to shut down the still in the evening without drainage of the liquid on the plates in the column back to the still pot when this cools, as thereby fractions which are already separated would be mixed. An intermittent adding of liquid to the still pot during a distillation also tends to start the siphoning of liquid from the column to the still pot due to the cooling of the liquid in the still pot. In industrial stills that operate continuously the liquid is preheated and carefully added to the still pot at a continuous, uniform rate, which would be impracticable in this problem because a preheating of the oil would increase the possibilities of cracking. For these reasons rectifying columns with non-siphoning bubbling cap plates have been developed and are described in the accompanying figures. In the column shown in Fig. 2 the ascending vapor normally follows the path of the arrows, passing up through the vapor tube in the center of the plate, then dowr along the inside wall of the bubbling cap. Near the bottom of the bub bling cap the vapor is forced out through a series of small holes. The liquid is thoroughly agitated by the stream of fine bubbles passing through it. When condensed liquid fills the plate above a certain level it overflows through *B*. In order to maintain an even distribution of the vapor through the holes in the bubbling cap, this must be coaxial with the vapor inlet tube. A simple method of accomplishing this is to ream the bottom of the bubbling cap to fit the tapered portion of the vapor inlet tube (or a loose tapered ring) as shown in Fig. 2.

In order to prevent the siphoning of liquid through *A*, the height of

the bubbling cap has been increased, so that the vapor inlet tube extends above the level of the liquid on the plate by an amount somewhat greater than the depth of the liquid seal on the plate below. Referring to Fig. 2, H_1 has been made considerably larger than H_2. This provides a path for the vapor to pass downward in the column through B whenever the tendency to siphon occurs. Hence in a column of this type the plates will always remain completely filled with liquid.

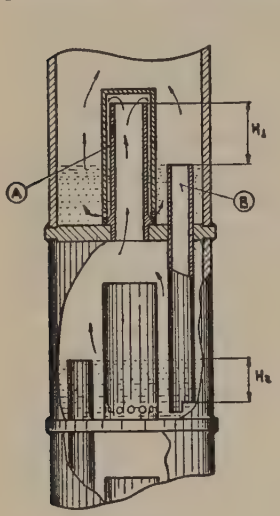

Fig. 2

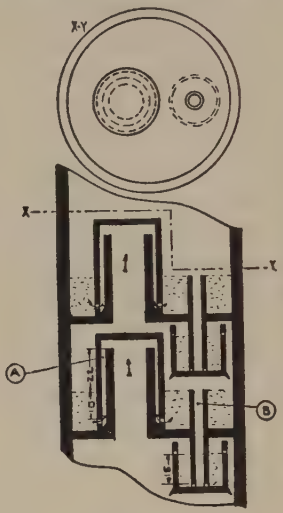

Fig. 3

Fig. 4

Fig. 2. Non-siphoning Bubbling Cap Plate with the Liquid Seal on the Plate

Fig. 3. Non-Siphonong Bubbling Cap Plate with the Liquid Seal Located between the Plates

Fig. 4. Non-Siphoning Bubbling Cap Plate Combining the Bubbling Cap with the Reflux Drain

The bubbling cap plate shown in Fig. 3 is based upon the same principle as that shown in Fig. 2, the difference being the fact that the liquid seal is kept separated from the plate below. Whenever vapor passes downward through the seal a small amount of liquid is removed from the seal. The dimensions must therefore be properly adjusted so that, after this loss, the amount of liquid remaining is large enough to prevent any vapor from passing upward through B.

In Fig. 4 is shown a combined reflux drain and bubbling cap plate which is non-siphoning. This design differs from the designs in Figs.

2 and 3 in that vapor passes downward, not through the liquid seal but through the bubbling cap itself. This has been accomplished by making the capacity of *A* larger than the volume of all the liquid on the corresponding plate when in operation. When tendencies to siphon occur the liquid on the plate will at first be sucked into the large bubbling cap *A* which will be only partly filled. The vapor can then bubble backward through this liquid. A plate column of this particular design has not

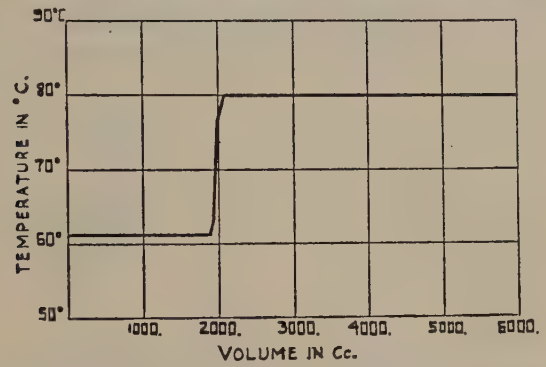

FIG. 5. VOLUME-TEMPERATURE DISTILLATION CURVE FOR A 20 PLATE RECTIFYING STILL

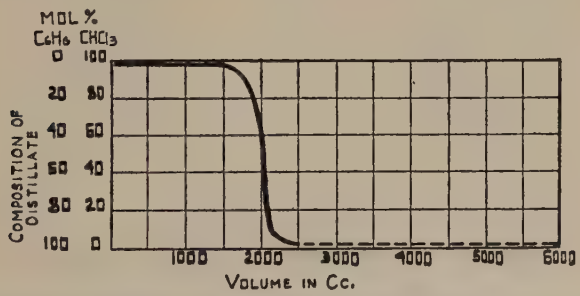

FIG. 6. VOLUME-COMPOSITION CURVE FOR A DISTILLATION IN A 20 PLATE RECTIFYING STILL

been built but it should work satisfactorily for laboratory separations in which a relatively low rate of distillation is employed. If high rates of distillation were employed the space within which the bubbles rise through the liquid might have to be increased.

A 20-plate rectifying column of the type shown in Fig. 2 has been built (see section V) and found to work very satisfactorily. In order to test the heating system and auxiliary apparatus of this still, it was charged with a mixture of 2 liters of $CHCl_3$ and 4 liters of C_6H_6, and a preliminary

distillation was carried out. The results of this run are shown in Figs. 5 and 6. Fig. 5 shows the temperature-volume curve for the distillation and Fig. 6 shows the composition of the distillate in mole per cent plotted against the volume of each fraction. About 1500 cubic centimeters of the chloroform came over a concentration of about 98 mole per cent. As indicated by the dotted line in Fig. 6 the distillation was discontinued when 2500 cubic centimeters of distillate was obtained.

Fig. 7 shows a non-siphoning bubbling cap column which has been developed for rectifying stills of glass. A column consisting of two

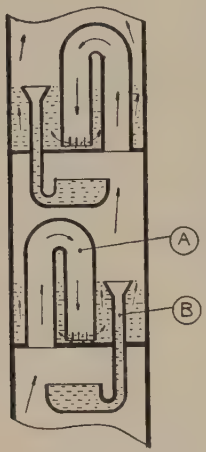

FIG. 7

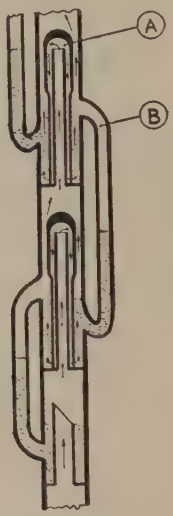

FIG. 8

FIG. 7. NON-SIPHONING RECTIFYING PLATE CONSTRUCTED OF GLASS
FIG. 8. NON-SIPHONING RECTIFYING PLATE CONSTRUCTED OF GLASS

plates of this design has been made with an outside diameter of 35 mm. and found to work satisfactorily. For columns of smaller diameters, however, this type has the disadvantage that the return of liquid through *B* does not take place as readily as it should and the column tends to "flood" except when slow rates of distillation are employed. It is evident that the dimensions of the drain tube *B* are limited by the same relations between the reflux drain and the cup below as mentioned in the description of Fig. 3.

A glass-rectifying column which is entirely free from the objections mentioned above is shown in Fig. 8. This type is comparatively easy

to make as the vapor inlet tube is simply flanged at one end and then sealed directly to the column. The bubbling cap is loose and is provided with six narrow slits (made by grinding on a carborundum disc wheel) for the purpose of breaking up the bubbles. The reflux drain *B* is located outside the columns and can be made large enough to take care of any rate of reflux which may be desired. The diameter of a column of this type is not subject to any limitation concerning size, and should therefore work satisfactorily even for a column with a "hold up" of only a few tenths of a cubic centimeter per plate or less. A rectifying still consisting of 10 plates of the type shown in Fig. 8 has been made (see section VI) and is being used successfully for distillation at different speeds and with different liquids. When distilling a mixture of 50 mole per cent $CHCl_3$ + 50 mole per cent C_6H_6, all but the last 50 cubic centimeters of the $CHCl_3$ distilled over as 99 mole per cent. Using the same mixture and the same rate of distillation in a column of the same length filled with steel "jack chain," the best efficiency obtained at any time was $CHCl_3$ at 94 mole per cent.

IV. REFLUX REGULATORS FOR LABORATORY STILLS

For a continuous distillation it has been shown[12] theoretically that the reflux ratio[13] must always be maintained above a certain minimum value, in order to obtain a certain degree of fractionation. The theoretical calculation is a more difficult one for the ordinary laboratory rectifying still (batch still) in which the composition of the liquid in the different parts of the system is continually changing during the distillation. However, it is generally agreed that a high efficiency of separation is obtained by using a large reflux ratio and a small rate of distillation.[14] For the purpose of controlling the reflux ratio and indicating the rate of distillation, the following reflux regulators have been developed. They are modifications of a type which is used on industrial stills and they give a reflux ratio which is independent of the rate of distillation. Fig. 9 shows a reflux regulator for use on stills for which a definite and constant reflux ratio is desired. Fig. 10 shows a reflux regulator which permits a wide range of reflux ratios.

[12] W. K. Lewis, Ind. Eng. Chem., **14**, p. 492; 1922, and the literature there cited.

[13] The reflux ratio is the number of mols of vapor returned as refluxed liquid to the column per unit time divided by the number of mols of final product obtained per unit time.

[14] Shirk and Montonna, Ind. Eng. Chem., **19**, p. 907; 1927, and the literature there cited.

Referring to Fig. 9, the vapor leaves the rectifying column at A. By means of a reflux condenser B it is completely condensed into the bulb C. From the bottom of this bulb a certain part of the condensate is returned to the column through the capillary tube R. Another part of the condensate passes through the capillary tube D into the cooler H and to the receiver.

In order to obtain a definite and constant reflux ratio the capillary tubes R and D are made of the same bore but their lengths are made indirectly proportional to the amounts of liquid they should carry. For instance if $R = 5$ and $D = 50$, the volume of reflux returned to the col-

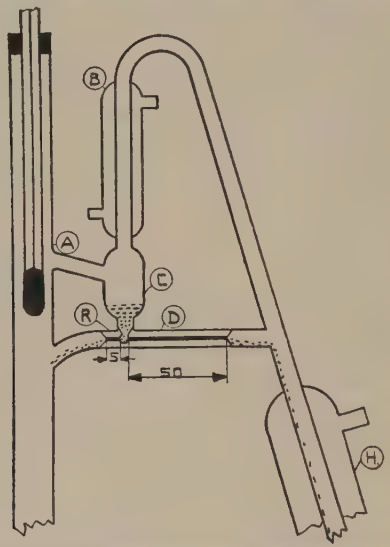

FIG. 9. REFLUX REGULATOR FOR MAINTAINING A DEFINITE AND CONSTANT REFLUX RATIO

umn divided by the volume of distillate will be 10. Instead of making the capillary tubes R and D of the same bore but of different lengths it may be preferred to have capillaries of different bores but of nearly the same lengths. In order to obtain the right lengths of the two different sizes of capillary tubes these are sealed horizontally to a vertical glass tube. Liquid is then allowed to run through the T-tube and the flow per unit time is measured for both capillaries. The capillary tubes are then gradually shortened until the desired amount of liquid per unit time will run through each of them. The T-tube is then sealed into the system and recalibrated.

The regulator in Fig. 9 will maintain a definite and constant reflux ratio at any rate of distillation. However, a flexibility in the reflux ratio during a distillation can be accomplished by placing an electric heating coil around the capillary tube *D*. This will cause an increase in the amount of flow through *D* by decreasing the viscosity of the liquid.

In addition to maintaining a constant reflux ratio during the distillation the reflux regulator is a convenient indicator of the rate of distillation, since this rate is directly proportional to the height of the liquid in the bulb *C*. This bulb may therefore be provided with a vertical scale on which each mark corresponds to a definite rate of distillation.

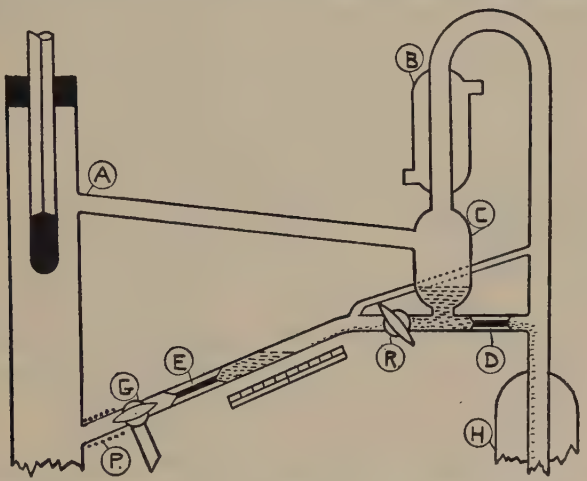

FIG. 10. REFLUX REGULATOR FOR A BOTH MEASURABLE AND VARIABLE REFLUX RATIO

Because of the fact that comparatively large amounts of vapor continually pass the thermometer bulb, constant temperature readings will be obtained, even for very small rates of distillation. An additional advantage is the complete elimination of all stopcocks in the reflux regulator.

Fig. 10 shows a reflux regulator for measuring and maintaining any desired constant reflux ratio. It is conveniently used on stills in which liquids of varied character are to be distilled. It may also be used for determining the most practical reflux ratio in problems involving extensive distillation. In Fig. 10 the vapor leaves the rectifying column at *A* and is condensed into the bulb *C*. A certain amount of the condensate is returned to the column through a stopcock *R* and a capillary flow-

meter E. Another part of the condensate is carried through the capillary tube D to the cooler H and to the receiver.

The proportion of reflux to distillate may be regulated as desired by adjustment of the stopcock R, and a quantitative measure of the reflux may be obtained at any time by observing the position of the liquid meniscus above the capillary E. This flowmeter is easily calibrated for any liquid by turning the 3-way stopcock G and collecting and measuring the liquid obtained during a short interval of time. With a given setting of stopcock R the position of the liquid meniscus above the capillary E is also a sensitive index of the rate of distillation. The tube which car-

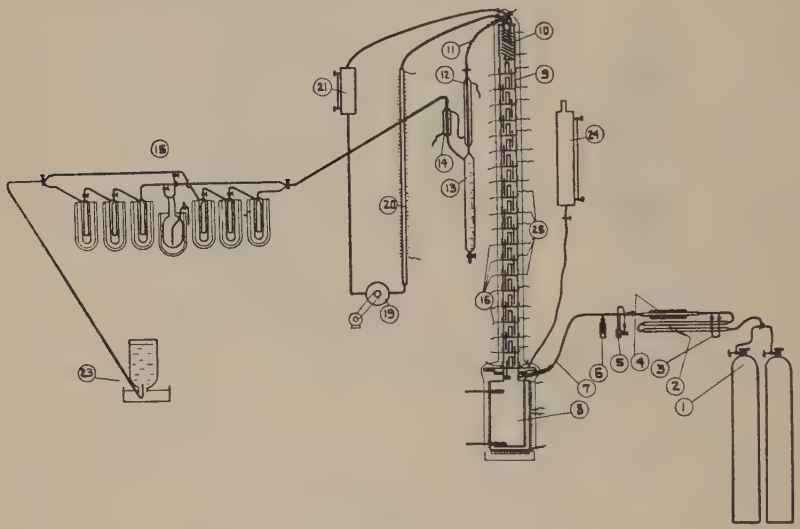

Fig. 11. Rectifying Still for Distillation in a Current of inert gas

ries the refluxed liquid back into the rectifying column should be surrounded by an electric heating coil P, in order to raise the liquid to its boiling point. If desired, the capillary tube D may be replaced by a stopcock, in order to give somewhat greater flexibility in reflux ratios but this introduces the disadvantage of contamination of the distillate by the stopcock lubricants.

As shown in Fig. 9 as well as in Fig. 10, there is a free and unconstricted passage between the vapor outlet A and the cooler H. Thus these regulators may be used for vacuum distillations as well as for distillations at atmospheric pressure. They have been used successfully with

bubbling-cap-plate columns of the type described in Fig. 8 as well as with iron jack-chain columns.

Acknowledgment is made to B. J. Mair for his helpful suggestions in developing this device.

V. A RECTIFYING STILL FOR DISTILLATION IN A CURRENT OF INERT GAS

The rectifying still, shown in Fig. 11, was developed in order to carry out efficiently the first distillation of the petroleum. The elements of the distillation train will be described in the order of passage of the inert gas from its storage cylinder to its final absorption (see Fig. 11).

(*a*) *The purification train.*—The CO_2 from its storage cylinder, *1*, passes first through two drying tubes, *2*, filled with "dehydrite" ($Mg(ClO_4)_2 \cdot 3H_2O$) and then through a U-tube flowmeter, *3*, filled with mercury. The top of each arm of the U-tube is blown out to a bulb in which baffle plates are inserted. (See flowmeter in Fig. 13.) This is to prevent the mercury from being blown out of the flowmeter if rates of gas flow should develop which exceed its capacity. The CO_2 then passes into a pyrex glass tube, *4*, filled with copper shavings and heated electrically to 650°C. (Preliminary experiments showed that at this temperature all traces of O_2 would be removed from the CO_2.) Glass or copper-to-glass seals are used for all connections in this part of the train.

(*b*) *The manometer and safety valves.*—The CO_2 from the furnace tube passes first through a cooling coil and then past a mercury manometer, *5*, and a safety valve, *6*.[15] The manometer registers the total pressure of the gas, which in turn is determined by the depth of liquid in the still pot plus that on the plates of the rectifying column. The safety valve acts with either increase or decrease of pressure to prevent any access of air to the gas stream. An automatic shut-off valve prevents any possible back flow of liquid from the still in the event of accidental interruption of gas pressure.

The CO_2 passes through a copper tube, *7*, (in Fig. 11) provided with an electrical heating coil. This tube is bent at the bottom of the still pot to form a large ring which is perforated so as to break up the gas flow into numerous streams of fine bubbles.

(*c*) *The still pot* (*8 in Fig. 11*).—The still pot holds about 20 liters. It is made of welded steel, and is joined to the column by a reinforced bolted flange sealed with a copper-ring gasket. The pot is provided

[15] For details see Fig. 2 of Bur. of Stds. J. of Research **2**, 471 (1929).

with two steel wells for thermocouples or thermometers. These are located about 5 and 30 cm. above the bottom. The pot is heated by three independent electric heaters, one at the bottom and two coiled around the cylinder. The still is charged at the beginning of the distillation as well as during a run by means of a filling device, *24*. This is a cylindrical brass tank provided with a sight glass and graduated in cubic centimeters. When the valve under the filling tank is opened the liquid flows by gravity through a copper tube to the still pot.

(*d*) *The fractionating column.*—The column, *9*, contains 20 non-siphoning bubbling cap plates of the design which was shown in Fig. 2. The bubbling caps and the centering rings are made of brass. All other parts of the column are made of steel and welded together. Each plate is provided with a well for a thermocouple. The thermocouples, by means of a multiple switch, are connected to a potentiometer. The column is heated electrically, independent heating coils, *25*, being used for each plate. The temperature is thus controlled by sliding rheostats, which are connected in series with each heating coil. The current to all of these heating elements is supplied through a main rheostat by means of which the temperatures of all of the plates may be increased or decreased in the same proportion. With these arrangements, together with the insulating covering of the column, any desired temperature condition may be maintained and it is also possible to clear the column at the end of the distillation. On the top of the column the dephlegmator, *10*, is located. The temperature of the dephlegmator (as indicated by thermocouples) is controlled by internal copper coils through which oil of desired temperatures is circulated by means of a special pumping and heating system, *19*, *20*, and *21*.

(*e*) *The condensers.*—The gas and vapor stream, after leaving the column, passes around a well containing a thermocouple and enters the first condenser, *12*, through a copper tube, *11*, provided with a heating coil to prevent the formation of a solid condensate. This tube is connected by a copper-to-glass seal to the inner tube of a vertical Liebig condenser, cooled by water of controlled temperature. The condensate from this condenser is received in the graduated tube, *13*, from the top of which the gas stream passes first through a water-cooled return condenser, *14*, and then through a series of condensers, *15*, of decreasing temperatures as follows: 0°, —15°, and —80°C. As indicated in Fig. 11, there are two independent trains of these low temperature condensers so that when the first is filled it may be shut out of the system and emptied by distilling into the large center bulb from which the condensate may be removed. In the meantime the second train is put into operation.

(*f*) *The CO_2 absorbers.*—From the last condenser of the train the gas passes through a saturated solution (*23*) of KOH which absorbs the CO_2, and the residual gases are collected in bottles over this solution.

VI. GLASS RECTIFYING STILLS FOR VACUUM DISTILLATION

For the purpose of subjecting the fractions obtained in the large rectifying still to further distillations a series of all-glass stills of successively

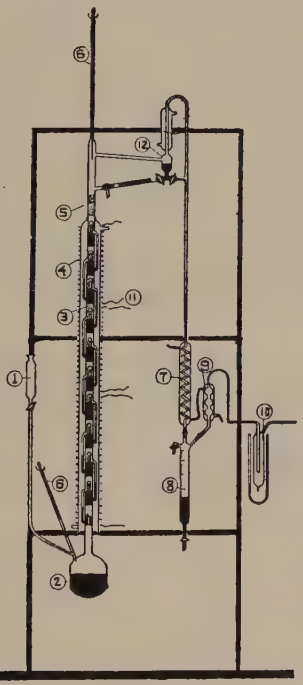

FIG. 12. RECTIFYING STILL OF GLASS WITH 10 NON-SIPHONING BUBBLING CAP PLATES

decreasing size have been developed. The rectifying columns of these stills are either non-siphoning bubbling cap columns or are columns packed with steel jack chain.[16]

An all-glass still of the first type is shown in Fig. 12. A filling tube, *1*, permits intermittent feeding of liquid into the still pot, *2*, without breaking the vacuum. The rectifying column, *3*, consists of ten pyrex glass

[16] Dean, Hill, Smith and Jacobs, Bureau of Mines, Bulletin 207, p. 9, 1922.

bubbling cap plates of the design previously described and shown in Fig. 8. The column is surrounded by an air jacket, *4*, through which air is circulated at a definite rate (as indicated by a flowmeter). Three thermometers are placed at different heights in the jacket and the temperature is regulated by three independent electric heating coils, *11*, which are wound around the jacket. Above the top plate, 15-cm. section of steel jack chain, is located (*5*). Thermometers are inserted at the vapor outlet and in the still pot and are inclosed as shown by *6*. No. *12* in Fig. 12 is the reflux regulator previously described in section IV. No. *7* is a Pyrex spiral condenser, and *8* a graduated receiver which is connected through a return condenser, *9*, a liquid air trap *10*, and an intermediate ballast (a 3-liter flask) to a mercury diffusion pump and McLeod gage. By closing the stopcocks between *7* and *8*, and *8* and *9*, and admitting CO_2 to the receiver, fractions can be withdrawn without breaking the vacuum in the still proper. The still is heated by an electrically heated bath of Nickel shot. This bath is a good conductor of heat, does not oxidize or smoke and at any time can be rapidly cooled by means of an airblast, which is forced down to the bottom through a copper tube.

Other types of rectifying stills have also been developed[17] and these are provided with air or vacuum jacketed columns which are packed with no. 20 steel "jack chain." In order to prevent oxidation or chemical changes of the jack-chain it has been chromium plated. Nickel or other platings may be used to serve the same purpose.

VII. APPARATUS FOR ORGANIC COMBUSTION ANALYSIS

In order to be able to determine the exact empirical formula for the hydrocarbons present in petroleum the apparatus shown in Fig. 13 has been developed. The essential feature in this apparatus is the fact that rubber connections, rubber stoppers and stopcock lubricant have been entirely eliminated, a fact which will increase the accuracy of the C and H analysis.[18]

Referring to Fig. 13, the oxygen after leaving the pressure regulator attached to the cylinder passes through a copper tube which is connected to the purification train by means of a ground copper-to-glass joint

[17] Bruun, Bur. of Stds. J. of Research, **2**, 476 (1929).

[18] For quantitative data relative to the magnitudes of the errors arising from the presence of (*a*) rubber connections, (*b*) stopcock lubricants, and (*c*) impurities in the oxygen, see Lindner (Ber. 60 B: p. 124; 1927) and the literature there cited.

(sealed with deKhotinsky cement). The flowmeter is provided with two bulbs with baffle plates to prevent the mercury from blowing out if excess pressures should develop accidentally. A tube of high melting Bohemian glass filled with 5 per cent palladium asbestos and heated electrically to redness serves to remove organic impurities from the oxygen. By means of two mercury seals this tube connects the flowmeter with the rest of the purification train, which consists of three successive tubes filled respectively with ascarite (for absorption of traces of CO_2), $CaCl_2$, and dehydrite ($Mg(ClO_4)_2 \cdot 3H_2O$), and P_2O_5 at the end of the purification train (to insure removal of the last traces of H_2O). The connection

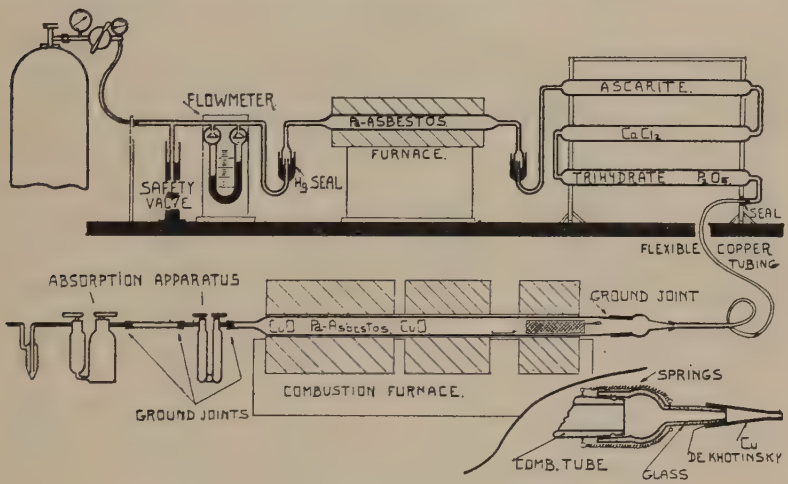

FIG. 13. APPARATUS FOR ORGANIC COMBUSTION ANALYSIS

between the purification train and the combustion tube consists of a flexible copper tube which is widened at each end and sealed to the glass by means of deKhotinsky cement.

The combustion tube (90 cm. long) is of Jena glass and filled with successive sections of copper oxide, palladium asbestos and copper oxide. To the inlet end of the combustion tube is fastened (with a specially designed ground joint held fast with springs) a Jena glass reducing collar. To the small end of this collar the copper line is sealed with deKhotinsky cement. The outlet end of the combustion tube is reduced and connected to the absorption apparatus by means of a ground joint. All the joints in the absorption apparatus are ground glass-to-glass and are sealed with Kroenig's micro cement which can easily be completely

removed by wiping with a cloth moistened with ether. The water absorption apparatus is filled with dehydrite and a small section of P_2O_5 at the end. The CO_2 absorber is filled with ascarite (and P_2O_5 at the end).

With the combustion apparatus described above a blank was run for 24 hours using the ordinary rate of oxygen and all the necessary manipulations. The results showed that the increases in weight of both the CO_2 absorber and the water absorber were below 0.2 mg. The results obtained with the apparatus (see Table 6) indicate that a combustion analysis of hydrocarbons can be duplicated with the following average

TABLE 6

Run	H	Deviation	C	Deviation	Sum
Combustion of resublimed naphthalene (not pure)					
	per cent		*per cent*		*per cent*
1	6.27	0.02	93.61	0.02	99.88
2	6.21	0.04	93.66	0.03	99.87
3	6.26	0.01	93.61	0.02	99.87
Average.....	6.25	0.023	93.63	0.023	99.87
Theoretical..	6.29		93.71		100.00
Combustion of a gas-oil fraction (liquid)					
1	13.66	0.02	86.10	0.03	99.76
2	13.64	0.00	86.05	0.02	99.69
3	13.61	0.03	86.08	0.01	99.69
Average.....	13.64	0.017	86.07	0.02	99.71

precision: Per cent C and H each to about ± 0.05. This makes it possible to determine with certainty the values n and x in the formula C_nH_{2n+x} for any hydrocarbon up to C_{100}.

VIII. DISTILLATION OF THE GAS-OIL FRACTION

The gas oil was at first distilled in the large rectifying still shown in Fig. 11. Before charging the still it was first assembled and tested for leaks by filling it with CO_2 at 25 pounds pressure and allowing it to stand for 15 days. At the end of this time the gage showed a pressure of 25 pounds. The still pot was then charged with gas oil to about three-fourths of its capacity. A stream of dry oxygen-free CO_2 at the rate of

150 cubic centimeters per minute was first bubbled through the oil for five hours at room temperature in order to remove dissolved air and water. The temperature of the still pot was then gradually raised until all of the plates of the column were filled as shown by the reading of the manometer. The heating coils of the plates were then adjusted so as to give a controlled gradient of about 70°C. between the bottom and top plates of the column. The temperature of the dephlegmator was set about 2° lower than the temperature of the upper plate. As distillation proceeded, the temperature of the still pot was raised from time to time, with corresponding adjustments of the column, until the temperature

TABLE 7

Distillation data

Serial number of fraction	Time		Temperature, top of column	Temperature, bottom of column	Volume of fraction
	hr.	*min.*	*°C.*	*°C.*	*cm³.*
3	6		107 to 221	About 306	910
4A	10	20	222 to 232	307 to 312	910
4B	13	40	233 to 237	313 to 316	565
5	16	40	238 to 252	317 to 321	845
6	19		253 to 267	322 to 327	875
7	20		268 to 274	328 to 330	860
8	23		275 to 279	230 to 335	860
9	31		280 to 285	336 to 344	890
10	32	20	286 to 301	345 to 351	910
Bottoms					7,800

of the liquid in the pot reached 350°C. Table 7 gives the results of the distillation.

The fractions obtained in the distillation in an atmosphere of inert gas were further subjected to a great number of repeated distillations under vacuum in smaller jack chain stills of glass. These distillations were carried out very slowly with a rate of the order of magnitude of 100 cubic centimeters an hour, and with intermittent addition of liquid to the still pot during the distillations.

When fractions having a constant boiling point were obtained, cooling curves were taken. Examples of these are shown in Fig. 14, where the break in the upper curve and the under cooling in the middle curve indicates that the fractions were approaching purity. A molecular

weight of this fraction and an organic combustion analysis indicated the formula $C_{18}H_{36}$. The physical properties of the fraction were:

Boiling point under high vacuum	152°C.
Freezing point	+6.5°C.
Refractive index at 20°C	1.468
Density 20°/4°C	0.839

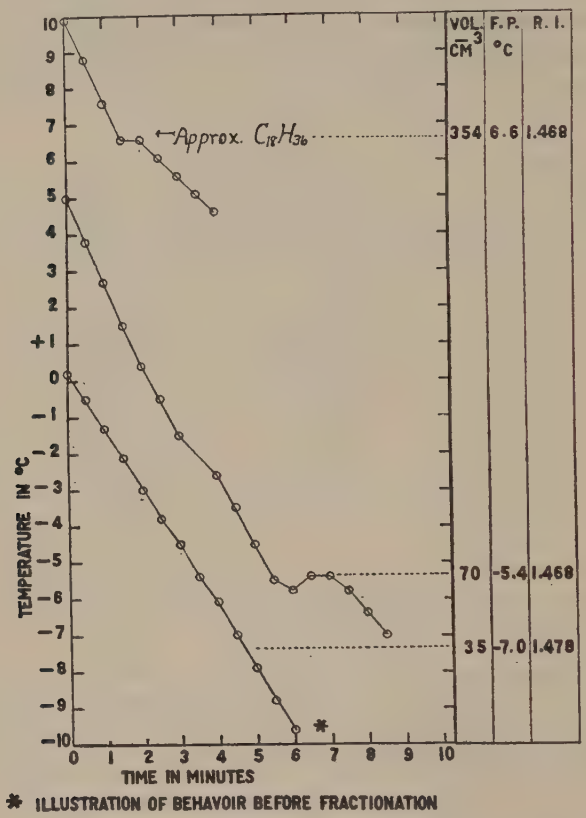

FIG. 14. SOME COOLING CURVES OF FRACTIONS SUBJECTED TO DISTILLATION

Several fractions were obtained, whose cooling curves indicated purity, but by means of crystallization methods these fractions were broken up into new ones. Although these new fractions did not differ much in their physical constants from those obtained by means of distillation, it was evident that the compounds were not as pure as desired. The

organic combustion analysis of the compound mentioned above, as well as a few others, together with their molecular weights gave an empirical formula having less hydrogen than would correspond to C_nH_{2n+2}. As, in addition, the iodine numbers proved the absence of unsaturated compounds, these results support the view that naphthene hydrocarbons are present in the higher petroleum fractions.[19]

The above results emphasize the necessity of having a large quantity of crude oil at the start if one hopes ultimately to obtain complete separation of the constituents of this petroleum.

IX. ISOLATION OF SOME OF THE ISOMERS OF HEXANE FROM PETROLEUM

The presence of all of the five isomers of hexane in petroleum has been proved. The usual methods of investigation have been combinations of distillation and strong chemical treatment, after which a mixture of hexane isomers has been obtained. By means of chlorination, bromination, or nitration of this mixture the corresponding derivatives of the hexanes have been obtained and, having larger differences in boiling points, these derivatives were separated by means of fractional distillation. Some investigators have attempted not only to prove the presence of these isomers but actually to isolate the compounds in pure condition by means of the above mentioned combination of distillation and chemical treatments. In this way Sidney Young[20] was able to isolate a small sample of n-hexane in fairly pure condition. With this exception, it seems that no one has been able to isolate either pure n-hexane or its isomers from petroleum.

In recent years other investigators, as Anderson and Erskin,[21] as well as Brown and Carr,[22] have separated some of the isomers by using efficient fractionating columns and without the aid of chemical reagents. Although the compounds obtained were not pure they are of higher purity than most of those which have been reported previously.

The possibility of obtaining pure hydrocarbons from petroleum by means of fractional distillation alone seems, in the writer's opinion, to depend entirely upon the crude oil used. If this contains cyclic compounds which form constant boiling point mixtures with the aliphatic hydrocarbons a complete separation can not be obtained. If, for in-

[19] Mabery, Proc. Amer. Acad., **37**, 565 (1902).
[20] J. Chem. Soc., London, **73**, 910 (1898).
[21] Ind. Eng. Chem., **16**, 263 (1924).
[22] Ind. Eng. Chem., **18**, 721 (1926).

stance, benzene is present, constant-boiling mixtures with the hexanes will be formed.[23] It is also possible that other ring compounds form constant-boiling mixtures with the isomers of the hexanes. As cyclic compounds as a rule have higher densities and refractive indices than the aliphatic hydrocarbons, the ring compounds probably account for the fact that these physical constants always are found to be higher for the hexanes isolated from petroleum than for the corresponding synthetic ones. It is therefore desirable to develop a method for separating these cyclic from the aliphatic hydrocarbons.

In order to separate two liquids of similar boiling points, it is often desirable to add a third component which forms a constant-boiling mixture with one of the constituents, after which the mixture is distilled. A general application of this scheme would usually complicate matters owing to difficulties encountered in removing the added component after the distillation. If, however, this component is selected so that it can be extracted with water or some other suitable non-miscible liquid it gives a very convenient method for separating cyclic from aliphatic hydrocarbons.

In separating the ring compounds from the isomers of hexane a liquid such as absolute ethyl or methyl alcohol is added in certain proportions and the mixture is subjected to fractional distillation, after which the alcohol is extracted from the distillates with water, in which the hydrocarbons are insoluble. Ethyl alcohol forms with the isomers of n-hexane, mixtures of minimum boiling point. These minima are all below 58.68°C. On the other hand, constant-boiling mixtures of ethyl alcohol and ring compounds have boiling points somewhat higher, as indicated by the following data which are taken from International Critical Tables, Vol. III, p. 320:

"B" component	"A" component C_2H_5OH B.p.	Mole per cent of "A"
	°C.	
Cyclohexene	66.7	49.5
Cyclohexane	64.9	44.5
Methylcyclohexane	73	70
Benzene	68.24	44.8
1.3 cyclohexadiene	66.7	47.3
n-hexane	58.68	33.2

[23] Young, J. Chem. Soc., London, 73 (1898) trans. 922.

In the present investigation about 30 liters of a gasoline fraction (from No. 6 well of South Ponca Field, Kay County, Okla.), with a boiling point range of from about +34° to 180°C., was subjected to distilla-

TABLE 8

Compound	Boiling point corr. 760 mm.	Freezing point	Refractive index $n\frac{20}{D}$	Specific gravity 20°/4°C.
		°C.		
2-3 dimethylbutane				
(Ser. No. 114[3] = 40 cm³.)	58.0	−135	1.378	0.666
(Ser. No. 126[21] = 40 cm³.)	58.3		1.376	0.662
Synthetic according to I. C. T., Vol. I, p. 204	58.1	−135	1.378	0.666^{15}
According to Graham Edgar*	58.1		1.377	0.662
Beilstein Erg. 1, p. 55 (1928)	58.7^{762}			
2 methylpentane				
(Ser. No. 119[3] = 100 cm³.)	60.4		1.374	0.657
(Ser. No. 126[23] = 120 cm³.)	60.6	−143	1.373	0.655
Synthetic according to I. C. T., Vol. I, p. 204	60.0		1.372	0.654
According to Graham Edgar*	60.2		1.371	0.654
Beilstein Erg. 1, p. 53 (1928)			1.374	
3 methylpentane				
(Ser. No. 110[3] = 60 cm³.)	63.3	−118 ±5	1.376	0.665
(Ser. No. 127[3] = 50 cm³.)	63.2		1.375	0.660
Synthetic according to I. C. T., Vol. I, p. 204	64	—	1.377	0.668
According to Graham Edgar*	63.2	—	1.376	0.665
Beilstein Erg. 1, p. 54 (1928)	63.5–65.5		1.377	0.667^{20}
n-hexane (Ser. No. 126[35])	68.84		1.379	0.670
Synthetic according to I. C. T, Vol. I, p. 204	69.0	−94.3	1.376	0.660
According to Graham Edgar*	68.95	—	1.373	0.660
Beilstein Erg. 1, p. 51 (1928); p. 143 (1918)	68.95	−94.3	1.375	0.660

* Private communication.

tion by means of inert gas in the 20-plate rectifying still described in section V. Fractions having a boiling point range of 54° to 75°C. from this distillation were subjected to a great number of further fractional distillations in smaller glass stills described in section VI. These

distillations were alternated with distillations after the addition of a third component. As third components methyl and ethyl alcohol were used. During all these different types of distillation fractions having similar boiling points and physical constants were mixed and redistilled.

As a result of this investigation all the possible isomers of hexane have been isolated with the exception of 2-2 dimethylbutane, the boiling point of which (49.7°C.) lies outside the range of the fractions used for this investigation.

The physical constants determined for these fractions together with some of the most reliable data for the corresponding synthetic compounds are given in Table 8. The data on refractive indices and specific gravities given by other investigators have been rounded off.

The above compounds are, with the exception of the n-hexane, of a higher purity than any corresponding compounds previously isolated from petroleum.

SUMMARY

1. The change in iodine number of the "wax distillate" fraction of a petroleum oil produced by heating it for different periods and at different temperatures up to 370°C. in (*a*) air and (*b*) H_2, N_2, and CO_2, respectively, has been determined and it is shown that in the absence of air the rate of this change is greatly reduced, thus making it possible to distil petroleum at high temperatures without cracking.

2. For the purpose of investigating the possibility of subjecting petroleum fractions to a chemical treatment prior to the distillation, the effects of various chemicals upon the sulphur content and iodine number of the "raw wax" distillate and the gas oil fraction were investigated. Thus 100 per cent sulphuric acid gave the most satisfactory results for the purpose of removing sulphur compounds and unsaturated hydrocarbons, but as large quantities of the oils were removed and destroyed by this acid it was decided to carry out the distillation without previous chemical treatment.

3. The siphoning tendencies of previous bubbling cap stills have been avoided by constructing different types of metal, as well as glass, non-siphoning bubbling cap plates. These have the advantage that intermittent addition of cold liquid to the still pot can take place without allowing the liquid in the fractionating column to drain into the still pot. This increases the efficiency, as fractions already separated are not mixed again. Furthermore, an incomplete distillation may be shut down overnight or for the week-end without allowing the liquid on the plates to siphon into the still pot.

4. Reflux regulators have been developed for maintaining any definite reflux ratio independently of the rate of distillation. These regulators also serve as indicators for the rate at which the distillate is collected and may be used for distillations in vacuum as well as for distillations at atmospheric pressure. No stopcocks are located between the vapor outlet and the condenser.

5. A rectifying still with a column consisting of 20 non-siphoning bubbling cap plates and with means for independently controlling and measuring the temperatures of the plates has been constructed. The still is designed for distillation in a stream of inert gas (CO_2) with or without boiling. It is provided with a purifying train for the CO_2 with a series of condensers with temperatures stepped down to —80°C. and with final absorber for the CO_2.

6. A set of all-glass rectifying stills for vacuum distillation has been built. These stills have either non-siphoning bubbling cap plates or have columns packed with steel jack chain. The columns are vacuum or air jacketed and the stopcocks are mercury sealed. Provision is made for intermittent filling with liquid and withdrawal of fractions during the distillation. The still pot is heated by immersion in an electrically heated bath of nickel shot.

7. An apparatus for combustion analysis has been made with special provisions for purifying the oxygen employed, and with all rubber connections eliminated. With this apparatus the combustion analysis of a hydrocarbon can be duplicated with the average precision of about ± 0.05 per cent for both C and H. This makes it possible to determine with certainty the values of n and x in the formula C_nH_{2n+x}, for any hydrocarbon up to C_{100}.

8. By distillation of the gas-oil fraction a compound $C_{18}H_{36}$ was isolated. Although this compound was not as pure as desired, it supports the view that naphthene hydrocarbons are present in the higher petroleum fractions.

9. The fractions with a boiling point range of 58° to 70°C. have been subjected to extensive fractional distillation. A method of separating different types of compounds such as aliphatic from cyclic hydrocarbons has been developed. This is done by adding a water-soluble component such as an alcohol which forms a constant-boiling mixture with the aliphatic hydrocarbons. After the distillation water is added to the distillate whereby the insoluble hydrocarbons separate while the alcohol is extracted. Four of the five isomers of hexane have boiling points within 58 to 70°C. and all of these have been found and isolated in a fairly pure condition as indicated by the physical constants.

BIOGRAPHY

Johannes Hadeln Bruun, the author of this dissertation, was born November 8, 1899, in Ånge, Sweden. After having finished the elementary schools, 1905 to 1914, and Svenska Lyceum in Wiborg, 1914 to 1917, he attended the Institute of Technology in Helsingfors from 1917 to 1918. The year 1918 to 1919 he spent on practical work in chemical and mechanical industries, as required for entrance to the Norwegian Institute of Technology, in Trondhjem ("Norges Tekniske Høiskole") which institution he attended from 1919 to 1923, after which he received the degree: "Diplom Ingeniør." From 1923 to 1924 he worked in the chemical warfare service of the Norwegian Army. During the years 1924 to 1926 he was employed as analyst, research chemist, research assistant for technical director, plant chemist and head of manufacturing department at the American Aniline Products, Inc. During 1926 to 1927 he was in charge of a manufacturing department at the Amalgamated Dyestuffs and Chemical Works, and since January, 1927, he has been a research associate with Dr. E. W. Washburn chief chemist at the the Bureau of Standards. The author has been registered as a student at Johns Hopkins University since February, 1927.

PUBLICATIONS

In addition to his Diplom Ingeniør thesis which was published by Svante Arrhenius (Medd. K. Vetenskapsakad. Nobel Institut B. 6, No. 10 (1924)), the author has published the following papers:

1. A rectifying still for distillation in a current of inert gas (joint with Mildred M. Hicks). Bur. of Stds. J. of Research, **2**, 470 (1929).
2. The effect of high temperatures upon petroleum in the presence of hydrogen, nitrogen, or carbon dioxide. Bur. of Stds. J. of Research, **2**, 473 (1929).
3. Glass rectifying stills for vacuum distillation. Bur. of Stds. J. of Research, **2**, 476 (1929).
4. Apparatus for combustion analysis. Bur. of Stds. J. of Research, **2**, 487 (1929).
5. Laboratory rectifying columns with non-siphoning bubbling cap plates. Ind. Eng. Chem. Anal. **1**, 212 (1929).
6. Reflux regulators for laboratory stills. Ind. Eng. Chem. Anal, **2**, 187 (1930).
7. The isolation of some of the isomers of hexane from petroleum (ready for publication) joint with M. M. Hicks.